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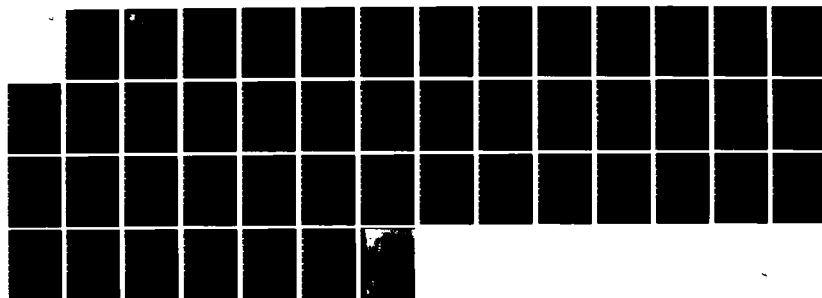
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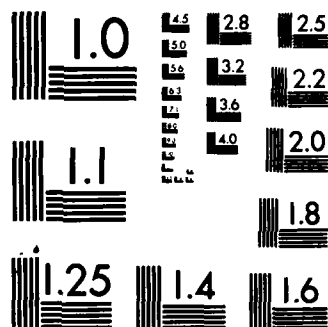
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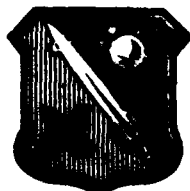
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for the period  
July 1983 to  
January 1984

## Spin-Polarized Triplet Helium

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April 1984

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## FORWORD

The work described herein was performed for the Air Force Rocket Propulsion Laboratory under MIPR RPL 39004. The project manager was 1Lt William A. Sowell. The program was carried out by Mr Jonas Stasys Zmuidzinas. This report has been reviewed and is released in accordance with the distribution statement of the cover and on the DD Form 1473.

  
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to produce He IV-M, and ultimately metallic He IV-A, by optically pumping the  $\text{He}_2^+$  species produced by electron bombardment of superfluid helium.

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ABSTRACT

T1 He\*

It is pointed out that bulk quantities of spin-polarized  $\text{He}^* = (2^3S_1)$  and  $\text{He}_2^* \equiv \text{He}_2(a^3\Sigma_u^+)$  should form insulating classical solids, respectively denoted as He IV-A and He IV-M. Estimates of some basic physical properties of He IV-A are given. A metallic phase of He IV-A is considered and modeled by a two-component Fermi fluid of spin-polarized  $\text{He}^{(+)}$  ions and electrons. This metallic phase is predicted to occur at  $\rho \approx 2.3$  and to lie considerably lower in energy than insulating He IV-A(M), making it the preferred phase to be looked for experimentally. A number of deexcitation mechanisms of atomic, dimerized, and bulk  $\text{He}^*$  are identified, and the open problem of stability is discussed. A method is proposed to produce He IV-M, and ultimately metallic He IV-A, by optically pumping the  $\text{He}_2^*$  species produced by electron bombardment of superfluid helium.

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## I. INTRODUCTION

States of matter characterized by large amounts of recoverable stored energy per unit mass are of great practical interest for obvious reasons. Well-known examples of such states are metallic hydrogen (MH)<sup>1</sup> and spin-polarized atomic hydrogen (H<sup>+</sup>).<sup>2,3</sup> Apart from practical applications such as energy storage, MH and H<sup>+</sup> are of intrinsic interest because of their predicted macroscopic quantum behavior, high-temperature superconductivity in the case of MH,<sup>4,5</sup> and low-temperature Bose-Einstein condensation in the case of H<sup>+</sup>.<sup>6,7</sup> In spite of some claims in the literature (see the review of Ref. 8), it is probably safe to say that MH has not yet been produced in the laboratory. The difficulty with MH is that very high pressures (> 1 Mbar) are required for production and very likely also for storage, since MH may be unstable at normal pressures.<sup>9-12</sup> In the case of H<sup>+</sup>, substantial concentrations have already been achieved using high magnetic fields (~ 100 kG) and sophisticated stabilization techniques.<sup>13,14</sup> Further progress in this field will depend on how well one will be able to control the various instabilities which lead to the recombination of atomic hydrogen into H<sub>2</sub>.

In this paper I shall discuss a novel energetic state of matter, denoted He IV,<sup>15</sup> which, like MH and H<sup>+</sup>, could be of considerable scientific and technical interest. Basically, He IV is a bulk aggregate of spin-polarized metastable triplet helium atoms (the He IV-A phase) or molecules (the He IV-M phase) of the abundant <sup>4</sup>He isotope with zero nuclear spin, the states in question being  $\text{He}(2\ ^3\text{S}_1) \equiv \text{He}^*$  and  $\text{He}_2(a\ ^3\Sigma_u^+) \equiv \text{He}_2^*$ .<sup>16</sup> As in the case of atomic hydrogen, spin polarization is essential for obtaining high concentrations of  $\text{He}^*$  and  $\text{He}_2^*$ , a prerequisite for forming He IV. The question of "existence" of He IV is really the question of lifetime, i.e., whether He IV is intrinsically sufficiently long-lived, or can be made such by appropriate external agents, in



order to be produced and studied experimentally. This question will be addressed in Sec. IV.

Unlike MH and  $H^+$ , which are quantum systems, He IV is predicted to be a classical solid at normal pressures, as will be discussed in Sec. II. Basically, He IV should exhibit properties similar to those of rare gas crystals, perhaps coming closest to solid argon as far as "quantumness" is concerned. What distinguishes He IV from rare gas solids is its magnetic, potentially ferromagnetic, nature.<sup>15</sup> It should be noted that a class of magnetic physical objects, including spin-polarized crystalline  $He^*$ , has been considered in 1976 by Smirnov and Shlyapnikov,<sup>17</sup> who called them metastable magnetic crystals. As will be discussed in Sec. II, some of their conclusions regarding  $He^*$  crystals are untenable in view of what is now known about the  $He^* - He^*$  potential.

Our study of He IV is in part motivated by the interesting question whether nonequilibrium macroscopic states of matter, such as bulk quantities of metastable electronically excited atoms and molecules, can be maintained or stabilized against reversion to the ground state for periods of time comparable to or longer than the natural lifetimes of isolated constituents. Metastable triplet helium is an especially attractive system for studying this stability problem because of its simple atomic/molecular structure and its very long radiative lifetime ( $\sim 2.5$  hours for  $He^*$  18-20). One can envisage several different ways how long-term stability of a nonequilibrium state might come about, for example, as a result of energy barriers to the ground state, collective effects in the condensed phase, external influences such as pressure, magnetic field, radiation field, etc. In Sec. IV we shall examine some of the mechanisms responsible for the decay of the excited state, leaving a detailed study of the stability problem for a future communication.

The paper is organized as follows. In Sec. II we discuss an atomic model of He IV and use it to estimate some properties of this substance on the basis of very simple calculations. A more fundamental model of He IV is introduced in Sec. III and used to discuss the behavior of He IV in the metallic regime. The problem of stability of He IV is discussed in Sec. IV. A possible method of experimentally producing He IV-M is discussed in Sec. V based on some previous unpublished work.<sup>21</sup> Finally, Sec. VI presents our conclusions and suggests some directions for further work in this field.

## II. ATOMIC MODEL OF HE IV

Throughout this section we shall be concerned with He IV-A, the atomic phase of He IV, commenting on He IV-M at the end.

Consider the static interaction of two isolated  $\text{He}^*$  atoms. The calculations of Garrison et al.<sup>22</sup> show that the potential curve for the  $^5\Sigma_g^+$  state of this system has an attractive minimum of 0.07 eV  $\sim$  812 K at 7.91 bohr<sup>23</sup> or 4.18 Å and, moreover, offer no suggestion of a repulsive hump at larger distances, as shown in Fig. 1. Thus an assembly of  $\text{He}^{*+}$  atoms would be expected to form a crystal with a near-neighbor distance  $d \sim 4.2$  Å, somewhat larger than that of solid helium ( $\sim 3.68$  Å for the hcp phase of  $^4\text{He}$ <sup>24</sup>). This conclusion is at variance with the estimate of Smirnov and Shlyapnikov,<sup>17</sup> who give  $d \sim 6.98$  Å. The reason for this large value of  $d$  is that they have based their calculations on an asymptotic form of the quintet potential which does not represent correctly the features of the actual potential in the region of its minimum. Corresponding to our value of  $d$ , we can estimate the number density of He IV-A as  $d^{-3} \sim 1.3 \times 10^{22} \text{ cm}^{-3}$  compared with  $2.2 \times 10^{22} \text{ cm}^{-3}$  for liquid helium.

It is important to note<sup>22</sup> that the  $^5\Sigma_g^+$  state of two  $\text{He}^{*+}$  atoms is a bound, nonautoionizing state because  $\text{He}_2^+$  and an electron can only form singlet and triplet continua. One can generalize this result and show that the  $J = n$  state of  $n$   $\text{He}^{*+}$  atoms is nonautoionizing for any  $n > 1$ . If this were not the case, there would be no chance of forming He IV-A.

The 812 K minimum of the  $\text{He}^*$  quintet potential noted earlier is much deeper than that of any rare gas pair potential, the most extreme case being xenon whose pair potential is known to have a depth of 228 K.<sup>25</sup> This suggests that He IV-A should be a very classical solid. Before drawing such a conclusion, however, one should take into account the fact that the atomic mass of helium is much smaller than that of xenon. The quantumness of a solid may be more

reliably determined by computing its dimensionless de Boer quantum parameter<sup>25</sup>

$$(2.1) \quad \Lambda = \hbar / \sigma (m \epsilon)^{1/2},$$

where  $\sigma$  is the hard-core radius [value of  $r$  at which the pair potential  $V(r)$  first decreases to zero],  $m$  is the atomic mass, and  $\epsilon$  is the potential depth. One usually employs (2.1) in conjunction with the Lennard-Jones 6-12 potential. The quintet  $\text{He}^*$  pair potential of Garrison et al.<sup>22</sup> is not quite of this type<sup>26</sup> but, nevertheless, a rough estimate of  $\Lambda$  based on (2.1) should be illuminating. With  $\epsilon = 0.07$  eV and the estimate  $\sigma = 6.2$  bohr, we find

$$(2.2) \quad \Lambda(\text{He}) \approx 11.4 \quad \Lambda(\text{He}^*) \approx 14.6 \quad \Lambda(\text{Ar}).$$

Thus He IV-A is roughly eleven times less quantum than solid helium or just a bit more quantum than solid argon.

Having ascertained that He IV-A is a classical solid, similar to solid argon in its quantumness, we may wish to estimate its melting temperature. From the data assembled by Guyer<sup>25</sup> and partially reproduced in Table I, we note that for rare gas solids the ratio of  $\epsilon$  to  $T_m$ , the melting temperature, is essentially constant, independent of the atomic mass. On the basis of this empirical fact, we can make the estimate

$$(2.3) \quad T_m(\text{He IV-A}) \approx 815 \text{ K} / 1.4 \approx 580 \text{ K}.$$

Thus, if otherwise sufficiently long-lived, He IV-A should be thermally stable, as a crystal, well above room temperatures. Of course, at the moment we cannot say anything about the effect of phonons on the electronic stability of He IV-A.

As is well known, rare gas solids have an fcc crystal structure. Calculations on the basis of assumed additivity of interatomic forces and using the Lennard-Jones 6-12 potential agree with experiment in showing that the fcc

structure has lowest energy.<sup>27</sup> Inasmuch as the form of the quintet He\* pair potential is different from Lennard-Jones, we cannot immediately say what the crystal structure of He IV-A should be. Calculations by Tapper<sup>28</sup> seem to show that fcc is the preferred structure for He IV-A, as for rare gas solids.

Without undertaking detailed calculations to determine the phonon spectrum we can still make a rough estimate of the Debye temperature of He IV-A using the method of Guyer.<sup>25</sup> His basic idea is to equate the energy of zero-point motion of an atom,

$$(2.4) \quad \epsilon_D \sim k_B \Theta_D \sim \hbar^2/m\langle u^2 \rangle_D,$$

to the dynamic energy

$$(2.5) \quad \epsilon_0 \sim \hbar(k/m)^{1/2}.$$

Here  $k_B$  is the Boltzmann constant,  $\Theta_D$  the Debye temperature,  $m$  the mass of He\*/He,  $\langle u^2 \rangle_D$  the mean square displacement of the atom, and

$$(2.6) \quad k = z V''(r_0)$$

the spring constant, where  $z$  is the number of near neighbors (= 12 for an fcc lattice), and  $r_0$  the location of potential minimum. From (2.4), (2.5), and (2.6) one gets

$$(2.7) \quad \Theta_D \sim (\hbar/k_B)[z V''(r_0)/m]^{1/2}.$$

We fit the data of Garrison et al.<sup>23</sup> to the following expression for  $V(r)$ , valid near the minimum of the potential:

$$(2.8) \quad V(r) \sim V(8) + (1/2) A (r - 8)^2 + (1/6) B (r - 8)^3.$$

The data in question are

$$V(7) = - 0.00224007,$$

$$V(8) = - 0.00259975,$$

$$V(9) = - 0.00209787,$$

with  $r$  and  $V$  in atomic units. The result of the fit is

$$A = 8.616 \times 10^{-4},$$

$$B = 4.266 \times 10^{-4}.$$

From these values we get

$$V''(7.91) = 8.232 \times 10^{-4} \text{ a.u.}$$

and then from (2.7), assuming an fcc structure for He IV-A,

$$(2.9) \quad \Theta_D(\text{He IV-A}) \sim 370 \text{ K.}$$

This fairly high value of  $\Theta_D$  reflects the relative steepness of the pair potential  $V(r)$  and the smallness of helium mass. To assess the reasonableness of this estimate, let us use the L-J potential

$$V_{L-J}(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$$

and the formula (2.7) to compute  $\Theta_D$  of argon for which  $\epsilon = 119.3 \text{ K}$ ,  $\sigma = 3.45 \text{ \AA}$ ,  $r_0 = 2^{1/6} \sigma = 3.87 \text{ \AA}$ , and  $m = 40 \text{ amu}$ .<sup>25</sup> One finds from

$$V_{L-J}''(r_0) = 72\epsilon/r_0^2 \approx 5.084 \times 10^{-4} \text{ a.u.}$$

that

$$\Theta_D(\text{Ar}) \approx 0.248 \Theta_D(\text{He IV-A}) \approx 92 \text{ K},$$

in remarkable agreement with the experimental value 93 K.

Even though the pair potential for  $\text{He}_2^*$  is not available, one can make rough estimates of the properties of He IV-M on the basis of some reasonable assumptions about the  $\text{He}_2^*$  molecule. Because of the known small nuclear separation in  $\text{He}_2^*$  ( $\sim 2a_0$  or  $1.1 \text{ \AA}^{29}$ ) one can regard  $\text{He}_2^*$ , to a good approximation, as an excited (2s) electron moving in the potential of an almost pointlike  $\text{He}_2^+$  ion in its ground state. Similarly,  $\text{He}^*$  can be regarded as a bound state of a 2s electron and a ground-state  $\text{He}^+$  ion. The  $\text{He}^* - \text{He}^*$  and  $\text{He}_2^* - \text{He}_2^*$  potentials are primarily determined by the 2s electrons and should be very similar at distances  $r > 2a_0$  where the ionic structure effects are not too important. Thus, qualitatively, most of our conclusions about He IV-A should be roughly valid also for He IV-M after taking cognizance of the fact that  $\text{He}_2^*$  has twice the mass of  $\text{He}^*$ .

In conclusion, from the  $19.8 (18.1) \text{ eV}^{30}$  excitation energy of  $\text{He}^* (\text{He}_2^*)$ , we find that He IV-A(M) has a stored-energy capacity of  $474 (217) \text{ kJ g}^{-1}$ . By comparison,  $\text{H}^\dagger$  can store about  $215 \text{ kJ g}^{-1}$ , reflecting the  $4.5 \text{ eV}$  recombination energy of the reaction  $2\text{H} \rightarrow \text{H}_2$ . The figure for MH is close to that for  $\text{H}^\dagger$  but not quite firm because of uncertainties about the structure of MH.

### III. METALLIC HE IV-A

In the preceding section we have shown that at normal temperatures and pressures an assembly of  $\text{He}^{*+}$  would form a classical solid, He IV-A, with properties similar to those of rare gas solids. In particular, He IV-A is predicted to be an insulator. As before, leaving aside the difficult question of electronic stability, we wish in this section to discuss the possibility of a metallic phase of He IV-A.

A simple physical picture of an insulator-metal transition is that, as pressure is increased, the outermost electrons in the atoms composing an insulating solid are delocalized and become mobile or metallic. In the energy band picture, what happens is that the energy gap between the valence and conduction bands (2s and 2p in the case of He IV-A) is reduced to zero at the critical pressure  $P^*$  at which metallicity first occurs. This is the situation normally encountered, for instance, in MH. As we shall show below, the physical picture in the case of He IV-A is completely different.

For the purposes of discussing the behavior of He IV-A in the metallic regime, we shall regard He IV-A as a system composed of spin-polarized helium ions ( $\text{He}^{++}$ ) and spin-polarized electrons ( $e^{-+}$ ). Thus we shall be dealing with a two-component Fermi fluid, each component or species having but a single spin projection. It is clear that to discuss the stability question, one will have to generalize this model to include both spin projections for each species. This will be done elsewhere.

It is convenient to introduce a two-component Fermi field

$$(3.1) \quad \Psi(\vec{x}) = \begin{pmatrix} \chi_+(\vec{x}) \\ \psi_+(\vec{x}) \end{pmatrix} = \begin{pmatrix} \Psi_+(\vec{x}) \\ \Psi_-(\vec{x}) \end{pmatrix},$$

where  $\chi_+$  ( $\psi_+$ ) destroys an ion (electron) with spin up. The second-quantized



Hamiltonian for our model is then

$$(3.2) \quad H = \int d^3x (1/2) \nabla \psi^\dagger(\vec{x}) \cdot \mathcal{M}^{-1} \nabla \psi(\vec{x}) \\ + \int d^3x d^3y (1/2) : \rho_K(\vec{x}) V_{KK}(\vec{x} - \vec{y}) \rho_K(\vec{y}) :,$$

where colons denote normal ordering,

$$\mathcal{M}^{-1} = M^{-1} a_+ + m^{-1} a_-, \\ (3.3) \quad \rho_K(\vec{x}) = \psi^\dagger(\vec{x}) a_K \psi(\vec{x}), \\ a_K = (1/2)(1 + \kappa \tau_3),$$

$M$  and  $m$  are the ion and electron masses, and the Pauli matrix  $\tau_3$  acts on the space of the upper and lower components of  $\psi$ . The Hamiltonian (3.2) is phenomenological and includes only two-body interactions characterized by the potentials  $V_{KK}(\vec{x} - \vec{y})$ . The electron-electron interaction is pure Coulomb:

$$(3.4) \quad V_{--}(\vec{x}) = V_c(\vec{x}) \equiv e^2/|\vec{x}|.$$

The electron-ion and ion-ion interactions are Coulomb at distances large compared to the ionic radius  $r_i$ . At distances comparable to  $r_i$ , they should exhibit hard-core effects due to the Pauli exclusion principle in effect for the electrons. The magnitude of  $r_i$  is simply estimated as the radius of the first Bohr orbit of an electron in the presence of a nuclear charge  $+2$ :

$$(3.5) \quad r_i = \hbar^2/m(2e)^2 = a_0/4 \approx 0.132 \text{ \AA}.$$

As we shall see later, typical interionic distances in the metallic regime of He IV-A are about  $2.3 \text{ \AA} \gg r_i$ . Thus, to a good approximation, the ions may be regarded as pointlike and the interactions involving the ions as pure Coulomb:

$$(3.6) \quad V_{++}(\vec{x}) \approx V_c(\vec{x}) \approx -V_{+-}(\vec{x}) \approx -V_{-+}(\vec{x}).$$

The model Hamiltonian (3.2) thus becomes

$$(3.7) \quad H = \int d^3x \left( \frac{1}{2} \nabla \Psi^\dagger(\vec{x}) \cdot \mathcal{M}^{-1} \nabla \Psi(\vec{x}) \right. \\ \left. + \int d^3x d^3y \left( \frac{1}{2} V_c(\vec{x} - \vec{y}) \right) \right. \\ \left. \times :(\Psi^\dagger \tau_3 \Psi)(\vec{x}) (\Psi^\dagger \tau_3 \Psi)(\vec{y}) : \right.$$

In the metallic regime, with or without external pressure, He IV-A can be pictured as a simple metal consisting of a regular lattice of pointlike  $\text{He}^{++}$ , embedded in an inhomogeneous spin-polarized electron fluid. To estimate the ground-state energy of this system, we shall neglect inhomogeneities of the electron fluid and treat it as uniform. This is a reasonable approximation as long as we are not attempting to determine the crystal structure of metallic He IV-A for which purpose very accurate calculations of band-structure effects would be essential. In this paper we shall be content with a rough estimate of the metallic phase properties, leaving the more refined calculations for the future.

The ground-state energy for our system per ion-electron pair in the uniform electron-fluid approximation can be written as

$$(3.8) \quad E = E_M + E_e,$$

where  $E_M$  is the (Madelung) energy of the  $\text{He}^{++}$  lattice in the uniform negative background of the  $e^-$ , and  $E_e$  is the energy of the  $e^-$  fluid in a uniform positive background of smeared ionic charges. The Madelung energy is

$$(3.9) \quad E_M = - \frac{A_M}{r_s a_0},$$

where  $r_s a_0 = (3/4\pi n)^{1/3}$ ,  $n$  is the electron density, and the Madelung constant  $A_M$  for a number of crystal structures has been calculated by Sholl.<sup>31</sup> The largest value of  $A_M$  is for a bcc lattice:

$$(3.10) \quad A_M(\text{bcc}) = 1.791861.$$

Of course, this by no means implies that metallic He IV-A will actually have a bcc lattice structure; neglected band-structure effects must be computed in order to answer the delicate question of the energetically preferred lattice.

As shown by Hedin,<sup>32</sup> for a spin-polarized (ferromagnetic) state of electron fluid, one has the following expression for  $E_e$  in the random-phase approximation (RPA):

$$(3.11) \quad E_e = \beta^2(2.2099/r_s^2) - \beta(0.9163/r_s) + (1/2)E_c^{\text{RPA}}(\beta^{-4}r_s) \quad \text{Ry},$$

where  $\beta = 2^{1/3} \approx 1.260$  is a factor accounting for spin polarization, and the three terms on the right-hand side above represent the Hartree-Fock (HF) kinetic, HF exchange, and RPA correlation energies, respectively. The RPA correlation energy for unpolarized electron fluid is given as<sup>33</sup>

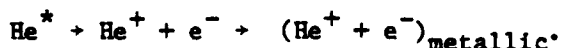
$$(3.12) \quad E_c^{\text{RPA}}(r_s) = 0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s - 0.036 r_s \quad \text{Ry}.$$

The total energy (3.8) for a bcc lattice is plotted in Fig. 2 and shows a minimum of  $-0.6859$  Ry at  $r_s \approx 2.3$ . For comparison, we also plot in Fig. 2 the total energy for an hypothetical (totally unstable) case of unpolarized electron fluid. Evidently, the position of minimal energy occurs at a smaller value of  $r_s$  ( $\approx 1.6$ ) for the unpolarized case. This fact can be interpreted as being the result of the Pauli exclusion principle in requiring a higher volume, other things being equal, for a spin-polarized electron fluid in order to minimize its energy.

In Fig. 3 we compare the energies of two bcc phases of He IV-A, the insulating and the (spin-polarized) metallic. The energy curve for the insulating phase is based on the results of calculations by Tapper.<sup>34</sup> Even considering that calculations of the RPA correlation energy are not very accurate

when  $r_s \geq 2$ , the evidence is overwhelming that the metallic phase is considerably lower in energy than the insulating phase for all values of  $r_s$ . This means that once a sufficient number of  $\text{He}^{*+}$  aggregate to form a speck of the insulating phase of He IV-A, there should occur a spontaneous phase transition to the energetically preferred metallic phase.

One can understand in a rough way why the metallic phase is the preferred one energetically. Note that  $\text{He}^*$  is 19.8 eV above the ground state and that the ionization energy for  $\text{He} \rightarrow \text{He}^+ + e^-$  is 24.6 eV. Thus it takes only  $24.6 - 19.8 = 4.8$  eV to ionize  $\text{He}^*$  (we neglect the small lattice binding energy in the insulating phase). On the other hand, the metallic binding energy of unpolarized  $\text{He}^+$  and  $e^-$  is about the same as that of a proton and  $e^-$ , namely 1 Ry or 13.6 eV (actually, Fig. 2 gives 0.94 Ry or 12.8 eV). The metallic binding energy of polarized  $\text{He}^+$  and  $e^-$  is somewhat smaller, about 0.68 Ry or 9.25 eV. Thus there is a gain of  $9.25 - 4.8 = 4.45$  eV per atom in the process



In conclusion, one can readily estimate the mass density of metallic He IV-A as  $0.89 \text{ g cm}^{-3}$  and the stored-energy capacity as  $324 \text{ kJ g}^{-1}$ .

#### IV. THE PROBLEM OF STABILITY

It seems to be the rule that aggregates of metastable excited constituents (atoms, molecules) have shorter overall lifetimes than the individual constituents in isolation. This is because in the bulk there can be present various perturbations, lattice imperfections, impurities, etc., which tend to shorten lifetimes of the excited constituents. There could conceivably be exceptions to the rule if, in the bulk, there were to exist collective effects tending to suppress the instabilities or decay mechanisms responsible for individual decays of the metastables. The possibility of an effect of this kind has recently been discussed by Manykin et al.<sup>35</sup> in their theory of the CES (condensed excited state). They consider condensation of excited atoms (in various levels of excitation) into a CES, much like the condensation or aggregation of  $\text{He}^*$  ( $\text{He}_2^*$ ) into He IV-A (M) discussed in our paper. Among other things, they argue that at high atomic excitations the resulting CES is characterized by a strongly inhomogeneous non-ideal electron liquid in which the many-body exchange and correlation effects conspire to make the CES lifetime longer than the lifetime of an isolated excited atom. If indeed genuine, such an effect would be most interesting. It is not a priori clear whether their arguments about the lifetime of the CES can be carried over to the case of totally spin-polarized electron liquid, of interest to us in connection with metallic He IV-A.

One can imagine several different ways He IV (or, more generally, an arbitrary CES) could be stabilized. First, it might be intrinsically stable, as a fortunate consequence of some collective many-body effect, under equilibrium (static) conditions in some regime of external parameters (temperature, pressure, static magnetic field, etc.). Failing this, He IV could conceivably be stabilized under nonequilibrium (dynamic) conditions by subjecting it to various kinds of external time-varying influences (electromagnetic radiation,

acoustic excitation, etc.). An intimate understanding of the physics of He IV will be needed in order to tackle the difficult and challenging problem of He IV stability. In this paper the best we can do is to identify some of the mechanisms leading to instabilities and loss of electronic excitation and so help focus one's attention on problems which require further study. We shall examine the decay mechanisms of increasingly complicated systems: first a single  $\text{He}^*$  atom, then a pair of  $\text{He}^*$ , and finally insulating He IV-A. The problem of the molecular species  $\text{He}_2^*$  is considerably more complex and will not be considered. It is believed that any insight gained into the atomic-species stability problem will also be useful for the molecular case. In any case, He IV-M may not merit too much attention because it may occur only as a transient phenomenon in the process of forming metallic He IV-A, as will be argued at the end of the next section.

#### A. An isolated $\text{He}^*$

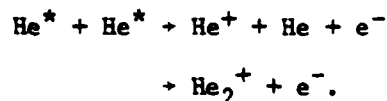
The lifetime of an  $\text{He}^*$  atom in isolation has been calculated<sup>36,37</sup> and later measured experimentally<sup>38</sup> as 2.5 hr. The reason for such a long lifetime is that the usually dominant fast electric-dipole (E1) process is strictly forbidden by spin conservation in the  $2\ ^3\text{S}_1 \rightarrow 1\ ^1\text{S}_0$  transition. The actual decay takes place via a slow relativistic magnetic-dipole (M1) transition. If this transition could somehow be inhibited,  $\text{He}^*$  would have a lifetime of about 8 years as determined by the next-dominant two-photon electric-dipole (2E1) transition.<sup>39</sup>

One can understand the physical reason for the slow M1 decay of  $\text{He}^*$  in the following way. The  $2\ ^3\text{S}_1$  state of the helium atom can be pictured as having two electrons with the same spin, say up, occupying the 1s and 2s orbitals. The 2s electron could lower its energy by making a transition to the 1s orbital but is prevented from doing this by the Pauli principle. The only way it can occupy

the 1s orbital is if it (or the 1s electron) first flips its spin. Now in the absence of spin-orbit (SO) and spin-spin (SS) interactions, spin is absolutely conserved and hence the 1s and 2s electrons will maintain their up-oriented spins indefinitely. Actually, the presence of small SO and SS interactions in the helium atom leads to spin disorientation and hence to the slow M1 decay.

### B. A pair of He\*

Consider a pair of He\* at close separations. Since He\* has spin one, the system of two He\* can have total angular momentum  $J = 0, 1$ , or  $2$ . Potential curves for the  $1, 3, 5\Sigma$  states of two He\* have been computed by Garrison et al.,<sup>22</sup> and their  $5\Sigma_g^+$  potential curve has already been used in Sec. II. The singlet and triplet  $\Sigma$  states are both autoionizing via the reactions

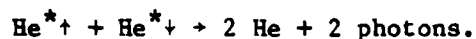


The detailed mechanism underlying the first of these reactions is illustrated in Fig. 4. The  $\text{He}_2^+$  molecular ion may be formed by direct electronic rearrangement or else as a result of attractive forces acting between  $\text{He}^+$  and He.

The quintet state of two He\* is nonautoionizing, as pointed out by Garrison et al.<sup>22</sup> and as discussed in Sec. II. Thus a pair of spin-polarized He\* should be able to bind, in view of the attractive  $5\Sigma_g^+$  potential, into a nonautoionizing dimer,  $(\text{He}^*)_2$ . Again, because of the existence of SO and SS interactions, the lifetime of such a dimer would be finite. In addition to the radiative decay channels for the individual He\*, there also exists the autoionizing decay channel for the dimer as a whole. The point is that the SO and SS interactions can cause a relative spin disorientation of the two atoms composing the dimer, thereby producing admixtures of singlet and triplet states and hence activating autoionization from these states. Without detailed calculations

it is difficult to say what the lifetime of the dimer could be.

In addition to the autoionizing reactions discussed above, two  $\text{He}^*$  with opposite spins can exchange two electrons and decay to the ground state by emitting two E1 photons:



This mechanism results in the release of  $2 \times 19.8 = 39.6$  eV of energy in contrast with the ionizing reaction in which the ejected electron has 15 eV of kinetic energy, reflecting the 24.6 eV ionization potential of helium.

### C. Insulating He IV-A

From the above discussion we conclude that, first, spin polarization is necessary but not sufficient in order to stabilize the  $(\text{He}^*)_2$  dimer against autoionization and, second, deexcitations of  $(\text{He}^*)_2$  occur as a result of the spin depolarization process, caused by the SO and SS interactions, activating the autoionizing or two-photon decays. It is not difficult to see that one can extend the argument to more than two  $\text{He}^*$  atoms and conclude that spin polarization is necessary, but probably not sufficient, for the stability of He IV-A, whether insulating or metallic. For the rest of this section we consider the simpler, insulating phase, even though the metallic phase is of actual interest but more difficult to analyze.

There is considerable similarity between the insulating phase of He IV-A and spin-polarized atomic hydrogen ( $\text{H}^\uparrow$ ), notwithstanding the fact that He IV-A is predicted to be a solid and  $\text{H}^\uparrow$  a gas. Both He IV-A and  $\text{H}^\uparrow$  are Bose systems and both are subject to deexcitation when opposite-spin atoms "recombine." One might expect that low-temperature magnetic stabilization against recombination



nature of total spin of the two systems. We recall that atomic H can be in a singlet or triplet state of total spin which is a combination of electronic and nuclear spins.  $\text{He}^*$  of course is pure electronic triplet, unless considered in conjunction with the singlet ( $2^1S_0$ ) excited state of substantially different energy. Much of the work in the literature<sup>40-43</sup> on the problem of stabilizing  $\text{H}^+$  could probably be adapted for He IV-A. But this might be a rather academic exercise in view of the primary interest in the energetically preferred metallic phase of He IV-A. The stability problem of this phase is complicated by the presence of itinerant electrons and is beyond the scope of this introductory paper.

# V. PRODUCTION OF HE IV-A

There is a considerable amount of experimental information showing that high-energy (10-100 keV or higher) electron bombardment of liquid helium is an efficient means of producing metastable excited helium atoms and molecules.<sup>44-49</sup> Although many different species of metastables are produced in these experiments, most of the species decay quite rapidly, and only the lowest-lying triplet atomic and molecular states,  $\text{He}^* = \text{He}(2\ ^3\text{S}_1)$  and  $\text{He}_2^* = \text{He}_2(a\ ^3\Sigma_u^+)$ , survive in larger concentrations for an appreciable length of time (e.g.,  $< 0.1$  s for  $\text{He}_2^*$ ).<sup>46</sup> The metastable populations achieved so far are of the order of  $10^{12}$  -  $10^{13}$   $\text{cm}^{-3}$ .

As explained in the last section, metastability of isolated  $\text{He}^*$  and  $\text{He}_2^*$  is due to the fact that electric-dipole transitions from triplet excited to singlet ground states are spin-forbidden. The metastable character of these species is apparently not much impaired when they find themselves in liquid helium. In fact, both absorption and emission spectra of the triplet excited species in liquid helium are remarkably similar to those of the species in free space. The explanation for this is that, as a result of repulsive forces acting between the excited electron in  $\text{He}^*$  or  $\text{He}_2^*$  and the surrounding helium atoms in the liquid, a cavity or bubble is formed around each excited atom or molecule, so that the latter finds itself in a relatively unperturbed environment.<sup>50</sup> As a consequence of this, the spin-nonconserving radiative lifetimes of  $\text{He}^*$  and  $\text{He}_2^*$  are not expected to be dramatically shortened by the presence of the surrounding liquid. Actually, the experimental evidence seems to be that the main destruction mechanism of triplet metastables in liquid helium is not radiative decay but bimolecular collisions in the case of  $\text{He}_2^*$  and  $\text{He}^*$ -to- $\text{He}_2^*$  conversion (via the reaction  $\text{He}^* + 2\text{He} \rightarrow \text{He}_2^* + \text{He}$ ) in the case of  $\text{He}^*$ .<sup>46,47</sup> The latter mechanism does not cause a loss of electronic excitation but simply

transfers the excitation from atomic to molecular species. The important conclusions of this discussion are that (i)  $\text{He}_2^*$  is the longest-lived metastable excited species in liquid helium and (ii) the dominant destruction mechanism of  $\text{He}_2^*$  in liquid helium is deexcitation in bimolecular collisions.

As discussed in the last section, a pair of  $\text{He}^*$  or  $\text{He}_2^*$  at small separations is unstable against autoionization and radiative decay via a two-electron exchange. Presumably, these are the mechanisms which are responsible for the bimolecular collisional destruction of  $\text{He}_2^*$  in liquid helium. By spin-polarizing the  $\text{He}_2^*$  sample in liquid helium, one should be able to suppress this destruction mechanism and hence achieve much higher  $\text{He}_2^*$  populations.

Successful suppression of the bimolecular collisional destruction mechanism presupposes that  $\Gamma_p$ , the rate of spin polarization, substantially exceeds  $\Gamma_C$ , the rate of collisional destruction:

$$(5.1) \quad \Gamma_p \gg \Gamma_C.$$

That is to say, an  $\text{He}_2^*$  sample must be spin-polarized rapidly enough before it is destroyed by collisions. The rate equation governing the decay of  $\text{He}_2^*$  populations of spin polarization  $\mu = 0, \pm 1$  (denoted by  $N_\mu$ ) due to bimolecular collisions is

$$\begin{aligned} (5.2) \quad \dot{N}_\mu &= - \sum_{\mu'} k_{\mu\mu'} N_\mu N_{\mu'} \\ &= - (\sum_{\mu' \neq \mu} k_{\mu\mu'} N_{\mu'}) N_\mu \\ &\equiv - \Gamma_{C\mu} N_\mu, \end{aligned}$$

where experiments give<sup>47</sup>

$$(5.3) \quad k_C \sim k_{\mu\mu'} (\mu \neq \mu') \sim 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (at 2.08 K).}$$

For a typical experimental situation with

$$N_{+1} = N_{-1} = N_0 = N/3,$$

$$N \approx 10^{12} \text{ cm}^{-3},$$

one obtains  $\Gamma = k_C N \sim 10^2 \text{ s}^{-1}$ .

In principle, it should be possible to spin-polarize  $\text{He}_2^*$  in liquid helium by means of strong magnetic fields at low temperatures. The problem, however, is that the rate of spin polarization  $\Gamma_p$  in this case is controlled by the spin-liquid relaxation time which is likely to be quite long because of the known small spin-rotation coupling in the  $\text{He}_2^*$  molecule. While the problem may not be too serious for low  $\text{He}_2^*$  concentrations (say,  $N \sim 10^{12} \text{ cm}^{-3}$ ), achieving orders-of-magnitude higher metastable concentrations might just not be feasible by means of the magnetic spin-polarization technique. For this reason, we next consider optical pumping as a method of spin-polarizing  $\text{He}_2^*$ . An important attractive feature of this method is that the rate of spin polarization is to a large extent controllable by the experimenter, by varying the pumping power.

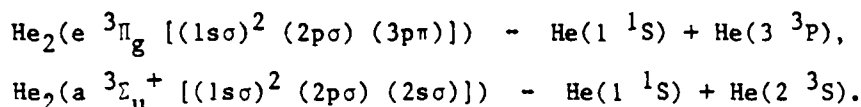
In order to select the upper state  $\text{He}_2'^*$  to which  $\text{He}_2^*$  is to be optically pumped, we look at Table 39 of Herzberg.<sup>51</sup> There are two states,  $e \text{ } ^3\Pi_g$  and  $c \text{ } ^3\Sigma_g^+$ , from which transitions to the metastable "ground state"  $a \text{ } ^3\Sigma_u^+$  are observed with "reasonable" wavelengths:

$$e \rightarrow a \text{ } (\lambda = 4650 \text{ \AA}),$$

$$c \rightarrow a \text{ } (\lambda = 9183 \text{ \AA}).$$

We shall choose  $\text{He}_2'^* = \text{He}_2(e \text{ } ^3\Pi_g)$  as the upper state of the optical pumping scheme because tunable dye lasers are readily available to pump the  $4650 \text{ \AA } e \rightarrow a$  transition. The  $c \rightarrow a$  pumping scheme might also be of interest if infrared lasers at  $9183 \text{ \AA}$  should become available.

In order to avoid complications of nuclear vibrations and rotations, we first discuss optical pumping of atomic triplet helium. In the united-atom limit for the helium molecule, one can establish the following correspondences between molecular and atomic states:



The transition of interest is thus  $3\ ^3P \leftarrow 2\ ^3S$ . Optical pumping of the  $2\ ^3P$  state in gas discharges has been investigated extensively.<sup>52,53</sup> The physics is basically the same whether one considers  $2\ ^3P$  or  $3\ ^3P$  as the upper state. The up- and down-transitions between the  $2\ ^3S_1$  and  $3\ ^3P_1$  states (we consider only  $J = 1$  for the upper state) are illustrated in Fig. 5 based on the assumption that 100 % circularly polarized light is used to pump the upper state and that all transitions are electric dipole (E1) and hence spin-conserving ( $\Delta m_S = 0$ ). Note that spin-orbit mixing in the upper state is essential in order for the optical pumping process to work in producing preferential population of the  $m_J = +1$  Zeeman sublevel in the  $2\ ^3S_1$  state.

The optical pumping rate is given as<sup>52</sup>

$$\Gamma_P = \sigma \phi,$$

where

$$\sigma \approx 2\pi \lambda^2 \approx 2.4 \times 10^{-10} \text{ cm}^2$$

is an estimate of the photon absorption cross section for the 3889 Å  $3\ ^3P \leftarrow 2\ ^3S$  transition, and  $\phi$  is the photon flux. Assuming a typical cw laser light beam of 1 mm diameter and 0.1 W power, we find

$$\phi \approx 2.5 \times 10^{19} \text{ photons cm}^{-2} \text{ s}^{-1}.$$

Thus

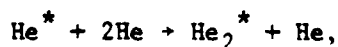
$$\Gamma_p \approx 6 \times 10^9 \text{ s}^{-1}.$$

This high value of  $\Gamma_p$  is effective only if there is substantial spin-orbit mixing taking place while the helium atom is in the P-state. The amount of mixing,  $\mu$ , can crudely be estimated by considering the product of the fine-structure energy (measure of spin-orbit interactions) and the lifetime of the P-state:

$$\mu \sim E_{fs} \tau / \hbar \sim (1 \text{ cm}^{-1}) (10^{-8} \text{ s}) / \hbar \sim 30.$$

Thus there is a large amount of mixing, and the pumping rate  $\Gamma_p$  should be fully effective. Note that  $\Gamma_p$  exceeds  $\Gamma_C$ , estimated earlier, by almost eight orders of magnitude. The inequality (5.1) is amply satisfied for metastable populations as high as  $10^{18} \text{ cm}^{-3}$  with the laser beam parameters chosen above. Of course, we have not taken into consideration various loss mechanisms which would tend to impair the efficiency of optical pumping. Moreover, in the actual case of interest one has to consider the effects of nuclear vibrations and rotations on the optical pumping process of molecular metastables. We shall now briefly examine this problem.

From the experiments of Keto *et al.*<sup>47</sup> one knows that there are basically two distinct mechanisms for producing  $\text{He}_2^*$  in liquid (actually, superfluid) helium. First, there is the direct production of ( $v = 0$ )  $\text{He}_2(a^3\Sigma_u^+)$  by bombarding electrons (and their secondaries). The second mechanism, already mentioned earlier, is indirect and operates via the reaction



where the  $\text{He}_2^*$  are produced in states of high vibrational excitation. Approximately the same number of  $\text{He}_2^*$  are produced in the  $v = 0$  level as in all

higher- $v$  levels. It appears that the ( $v > 0$ )  $\text{He}_2^*$  relax to the  $v = 0$  level within about 30  $\mu\text{s}$ .<sup>47</sup> From (5.2) and (5.3) we get

$$N(t) = N(0)[1 + k_C N(0)t]^{-1}.$$

If the initial population is  $\sim 10^{12} \text{ cm}^{-3}$ , then  $\Gamma_C = k_C N(0) \sim 10^2 \text{ s}^{-1}$  and the  $\text{He}_2^*$  sample is vibrationally relaxed to the  $v = 0$  level before much collisional destruction takes place. If, on the other hand,  $N(0) \sim 10^{18} \text{ cm}^{-3}$ , then  $\Gamma_C = k_C N(0) \sim 10^8 \text{ s}^{-1}$ . In this case the collisional destruction rate  $\Gamma_C$  is much larger than the vibrational relaxation rate  $\Gamma_v \sim (30 \mu\text{s})^{-1} \sim 3 \times 10^4 \text{ s}^{-1}$ . It now follows that by selective optical pumping of the  $v = 0$  level one will in general fail to pump the populated higher- $v$  levels of the  $a$ -state (because of transition frequency mismatching), and considerable collisional destruction of the  $\text{He}_2^*$  sample will occur as a result of the large  $\Gamma_C$ . It is unlikely that one can do much to increase the vibrational relaxation rate of  $\text{He}_2^*$  in liquid helium by artificial means.<sup>54</sup> In the interest of obtaining high concentrations of spin-polarized  $\text{He}_2^*$ , one might want to simultaneously optically pump a number of vibrational levels of  $\text{He}_2^*$ . It is not clear without detailed study how feasible such a multiple-pumping scheme would be in practice.

Let us now turn to the question how rotational excitations of molecules affect the optical-pumping process. The total angular momentum  $\vec{J}$  of a molecule is the sum of its total electronic spin  $\vec{S}$  and  $\vec{K}$ , the total angular momentum apart from spin. For  $\Sigma$  states  $\vec{K}$  is just  $\vec{N}$ , the angular momentum of nuclear rotation, perpendicular to the internuclear axis. In the case of the triplet states one has  $S = 1$  and  $J = K$ ,  $K \pm 1$ , except that  $J = 1$  for  $K = 0$ . The rotational spectrum of the  $a^3\Sigma$  state [Hund's case (b)] is therefore a series of  $K$ -levels, each of them split into three  $J$ -sublevels, except for  $K = 0$ . The rotational energies are given by

$$(5.4) \quad E_{\text{rot}} = B_v K(K+1) + O(\lambda),$$

where

$$B_{v=0} = B_e - \alpha_e/2 \approx 2.28 \times 10^5 \text{ MHz} \approx 7.6 \text{ cm}^{-1},$$

and the spin-spin constant  $\lambda$  determines the small (fine-structure) J-splittings.

Experiment gives<sup>55</sup>

$$|\lambda| \approx 1099 \text{ MHz} \approx 0.037 \text{ cm}^{-1}.$$

Because the  $^4\text{He}$  nuclei have zero spin and the electronic wave function of the  $a \ ^3\Sigma_u^+$  state is odd, the even-K rotational levels are missing for the (even)  $v = 0$  vibrational level.<sup>56</sup>

In the experiments of Keto et al.<sup>47</sup> it has been found that the odd K-levels 1 through 19 are populated in the ratios 100 : 12.8 : 4.5 : 5.0 : 6.4 : 6.0 : 9.0 : 6.4 : 4.8 : 2.5.<sup>57</sup> The percentage populations of these levels work out to be 63.5, 8.1, 2.9, 3.2, 4.1, 3.8, 5.7, 4.1, 3.0, 1.6. The important point is that the lowest  $K = 1$  level is almost two-thirds populated. This is fortunate because, as we now show, enhanced population of a single K-level is desirable in order to obtain maximal spin-polarization of  $\text{He}_2^*$ .

Suppose we optically pump the  $K = 1$  rotational level (we ignore the small J-splittings) of the  $a \ ^3\Sigma_u^+$  state to, say, the  $K = 1$  level of  $e \ ^3\Pi_g$ . Now the laser will also attempt to optically pump all the higher-K levels of the a-state. However, because of a mismatch between the corresponding K-level splittings of the a- and e-states ( $B_{v=0} = 7.60$  and  $7.17 \text{ cm}^{-1}$ , respectively), the laser, unless it has a broad linewidth, will "miss" the upper-state K-levels. What this means is that only the  $K = 1$  level will be spin-polarized, while the remaining K-levels of the a-state will remain unpolarized and will contribute to the destruction of  $\text{He}_2^*$ . Clearly, this undesirable state of affairs can



be remedied by either using broadband pumping or else, preferably, ensuring that only the lowest-K level of the a-state is heavily populated. In the case of thermalized rotational levels in liquid helium, operation at sufficiently low temperatures would certainly ensure this [note that  $\Delta E$  between the  $K = 1$  and  $K = 3$  levels is  $10 B_{v=0} \approx 110$  K, as determined from (5.4)]. For the non-thermal level population discussed earlier, the  $K = 1$  population is sufficiently enhanced, and so there should be no difficulty in obtaining considerable spin-polarization by optically pumping the  $K = 1$  level.

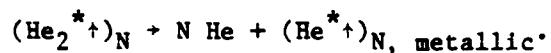
If sufficiently high  $\text{He}_2^{*\dagger}$  populations can be achieved by vigorous excitation of liquid helium and by judicious optical pumping of the molecular metastables, one might expect to observe novel phenomena, perhaps a transition to a new phase. Let us try to estimate the critical concentration,  $N_c$ , of  $\text{He}_2^{*\dagger}$  at which such a transition could be anticipated. We assume that the transition will occur when the  $\text{He}_2^{*\dagger}$  bubbles become closely packed and "burst." The nearest-neighbor distance of the bubbles in this case is  $2R_b$ ,  $R_b$  being the bubble radius. Assuming molecular and atomic bubbles to have roughly the same radii and taking  $R_b \approx 12a_0 \approx 6.35$  Å from the calculations of Hansen and Pollock,<sup>58</sup> we find

$$N_c \approx (2R_b)^{-3} \approx 5 \times 10^{20} \text{ cm}^{-3}.$$

It may well be that such high concentrations are actually not needed for the formation of the new phase, i.e., He IV-M. Thermal collisions between bubbles could lead to their coalescence as a result of attempts to minimize the total bubble surface energy. Once two  $\text{He}_2^{*\dagger}$  are inside a single bubble, the contraction of a dumbbell-shaped bubble to a spherically-shaped one will force the molecules to coalesce also. At intermolecular distances  $\sim 12a_0$  the quintet potential is already quite attractive and will provide a further impetus for

the  $\text{He}_2^{*\uparrow}$  to bind.<sup>59</sup> We see here a scenario for crystal formation of He IV-M in a possibly fairly dilute solution of  $\text{He}_2^{*\uparrow}$  in liquid helium. Undoubtedly, detailed analysis of the problem would be most illuminating.

Once a sufficient amount of He IV-M is formed, in the form of a micro-crystal, there should occur a spontaneous transition to the metallic phase of He IV-A by the reaction



This reaction is energetically favored because the loss of the 1.7 eV energy accounting for the binding of He and  $\text{He}^*$  into  $\text{He}_2^*$  is more than offset by the gain in energy in forming the metallic phase of He IV-A.

## VI. CONCLUSIONS

We have shown that attractive forces between spin-polarized  $\text{He}^* \equiv \text{He}(2^3\text{S}_1)$  will bind these species into a classical solid, He IV-A, with a nearest-neighbor distance of about 4.2 Å. The preferred crystal structure seems to be fcc.<sup>34</sup> The He IV-A solid is expected to be an insulator with Debye and melting temperatures about 370 K and 580 K, respectively. Its quantumness, as determined by the de Boer parameter, is on par with argon. The recoverable stored-energy capacity of He IV-A is 474 kJ g<sup>-1</sup>.

A metallic phase of He IV-A, modeled by a two-component Fermi fluid consisting of  $\text{He}^{+\uparrow}$  and  $e^{-\uparrow}$ , is shown to have a minimum of energy at  $r_s = 2.3$  corresponding to a mass density of 0.89 g cm<sup>-3</sup>. The metallic phase of He IV-A has a substantially lower energy than the insulating phase for all reasonable values of  $r_s$  and hence is the one expected to be realized in practice, if it possesses a sufficiently long lifetime. The stored-energy capacity of metallic He IV-A is still very high, about 324 kJ g<sup>-1</sup>.

In examining the question of stability, we have shown that spin polarization is absolutely essential in order to prevent destruction of He IV-A by autoionization or radiative decay. However, spin polarization may not be sufficient for stability because the spin-orbit and spin-spin interactions in helium lead to slow spin depolarization. As in the case of spin-polarized atomic hydrogen, it should be possible to stabilize the insulating phase of He IV-A in strong magnetic fields at low temperatures. However, because this phase is in any case unstable against transition to a metallic state, it does not seem worthwhile to devote too much attention to its stability problem. The problem of stabilizing the metallic phase is complicated by the fact that one must deal here with two species, ions and electrons, and that electrons are mobile. Nevertheless, recent work by Manykin *et al.*<sup>35</sup> suggests that there might exist collective

effects tending to stabilize condensed excited states (aggregates of excited atoms) beyond the lifetimes of individual excited constituents. These questions clearly deserve further study.

In the last section we have suggested that optical pumping of  $\text{He}_2^* \equiv \text{He}_2$  (a  $^3\Sigma_u^+$ ) produced in superfluid helium by electron bombardment might allow one to build up high concentrations of these species and to create microcrystals of He IV-M, a solid formed from spin-polarized  $\text{He}_2^*$ . We have also suggested that it might be energetically favorable for sufficiently large He IV-M microcrystals to make a transition to metallic He IV-A and shed their surplus ground-state helium atoms in the process. In this connection, it is appropriate to mention the work of Gspann and Vollmar<sup>60</sup> who have produced metastable excitations of large clusters ( $10^4$  to  $10^8$  atoms) of helium and neon by direct electron-bombardment of clusters formed in condensing nozzle flows.

#### ACKNOWLEDGEMENTS

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FOOTNOTES

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TABLE I. Some parameters of the rare gases. Here  $m$  is the atomic mass,  $\sigma$  the hard-core radius,  $\epsilon$  the potential depth,  $T_m$  the melting temperature,  $\Lambda$  the de Boer quantum parameter, and  $\Theta_D$  the Debye temperature.

Element	$m$ (amu)	$\sigma$ (Å)	$\epsilon$ (K)	$T_m$ (K)	$\epsilon/T_m$	$\Lambda$	$\Theta_D$ (K)
Ne	20	2.82	36.3	24	1.51	0.695	65
Ar	40	3.45	119.3	85	1.40	0.222	93
Kr	84	3.60	159	130	1.22	0.115	55
Xe	131	3.97	228	170	1.34	0.0846	72

# FIGURE CAPTIONS

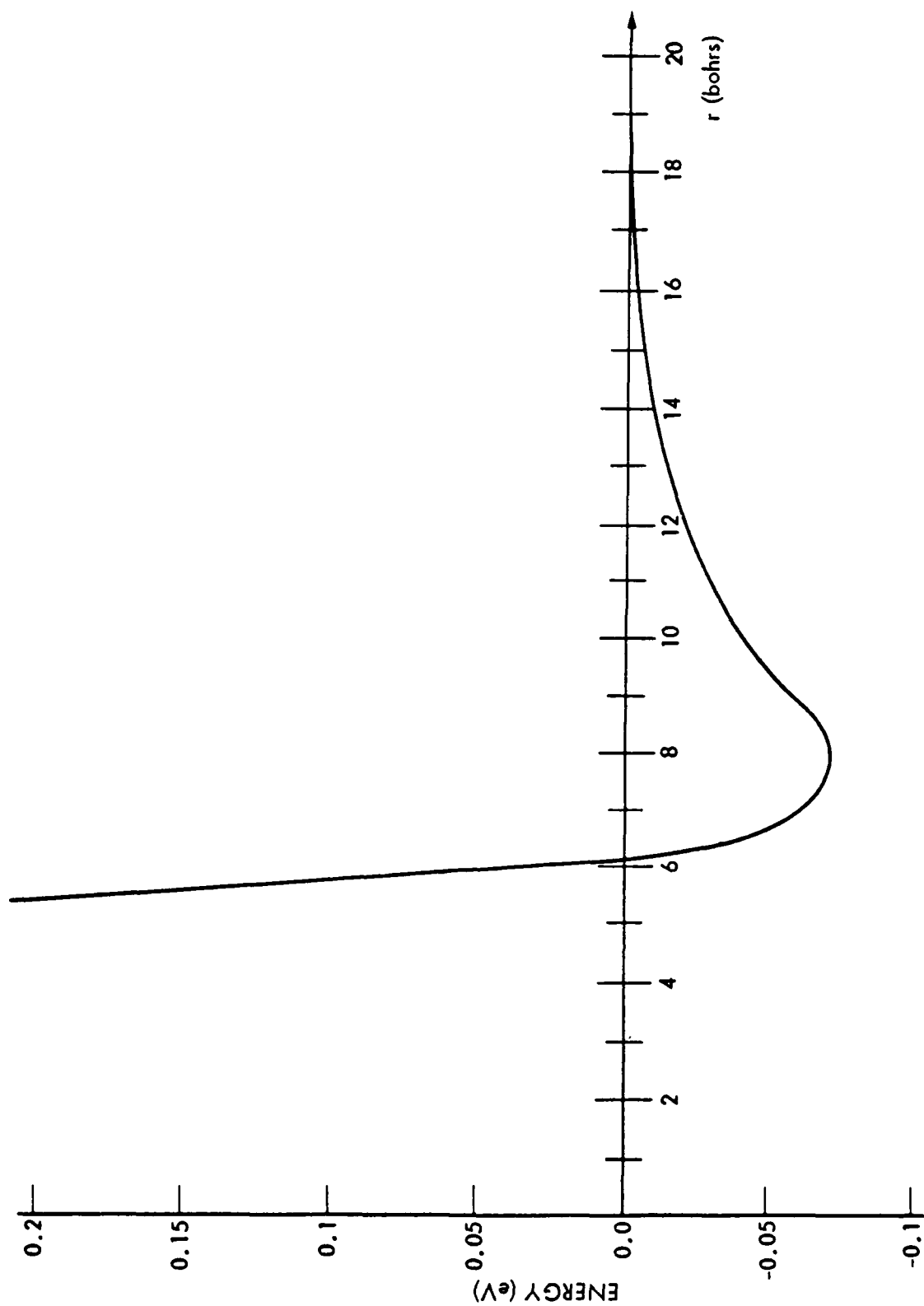
FIG. 1. The  $^5\Sigma_g^+ \text{He}^* - \text{He}^*$  potential curve from Ref. 22.

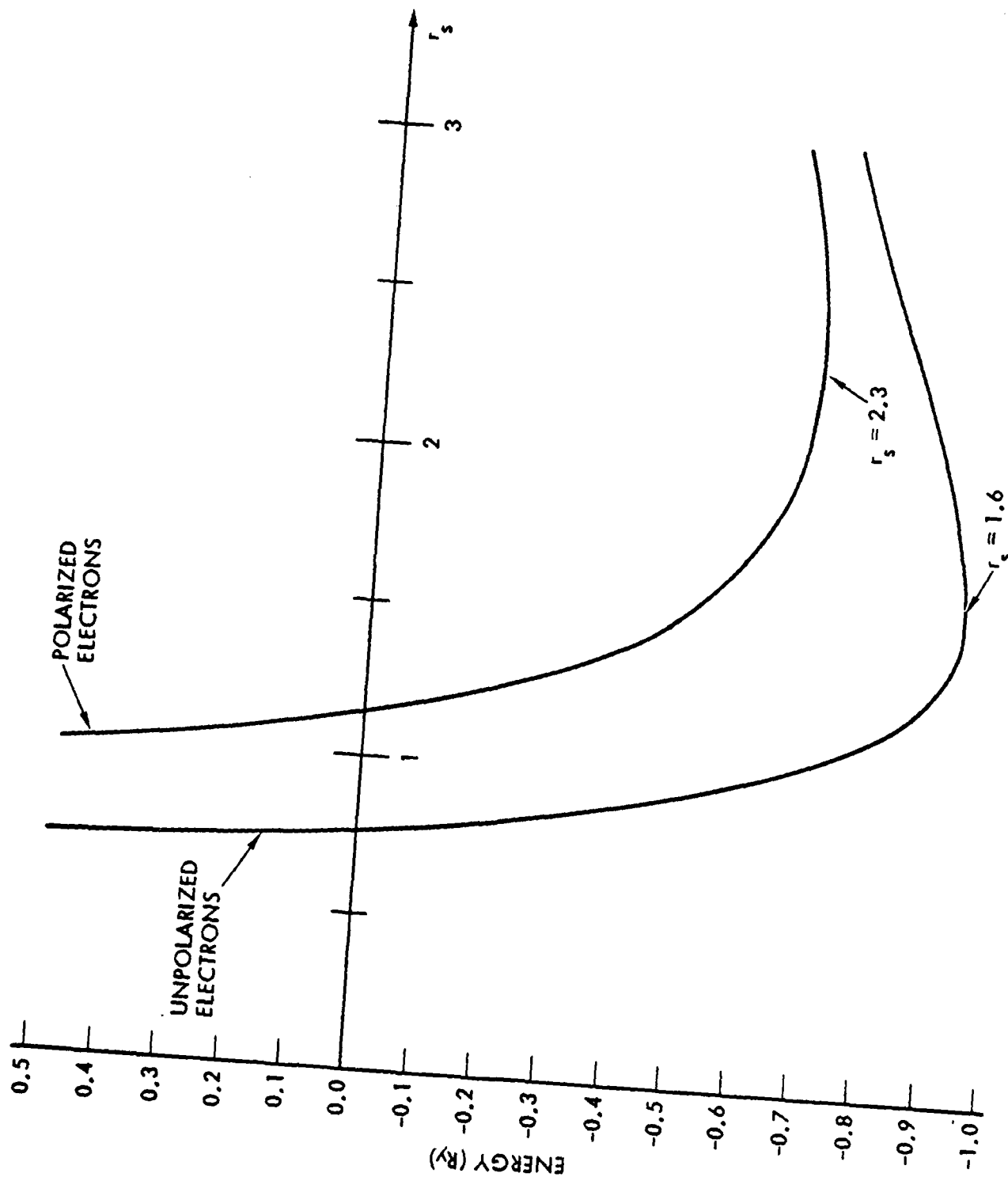
FIG. 2. The ground-state energy per ion-electron pair as a function of  $r_s$  for totally polarized and unpolarized electron fluid. The polarized-case energy is calculated from (3.11) as given. The unpolarized-case energy is calculated from (3.11) with  $\beta = 1$  and  $(1/2) E_C^{\text{RPA}} + E_C^{\text{RPA}}$ .

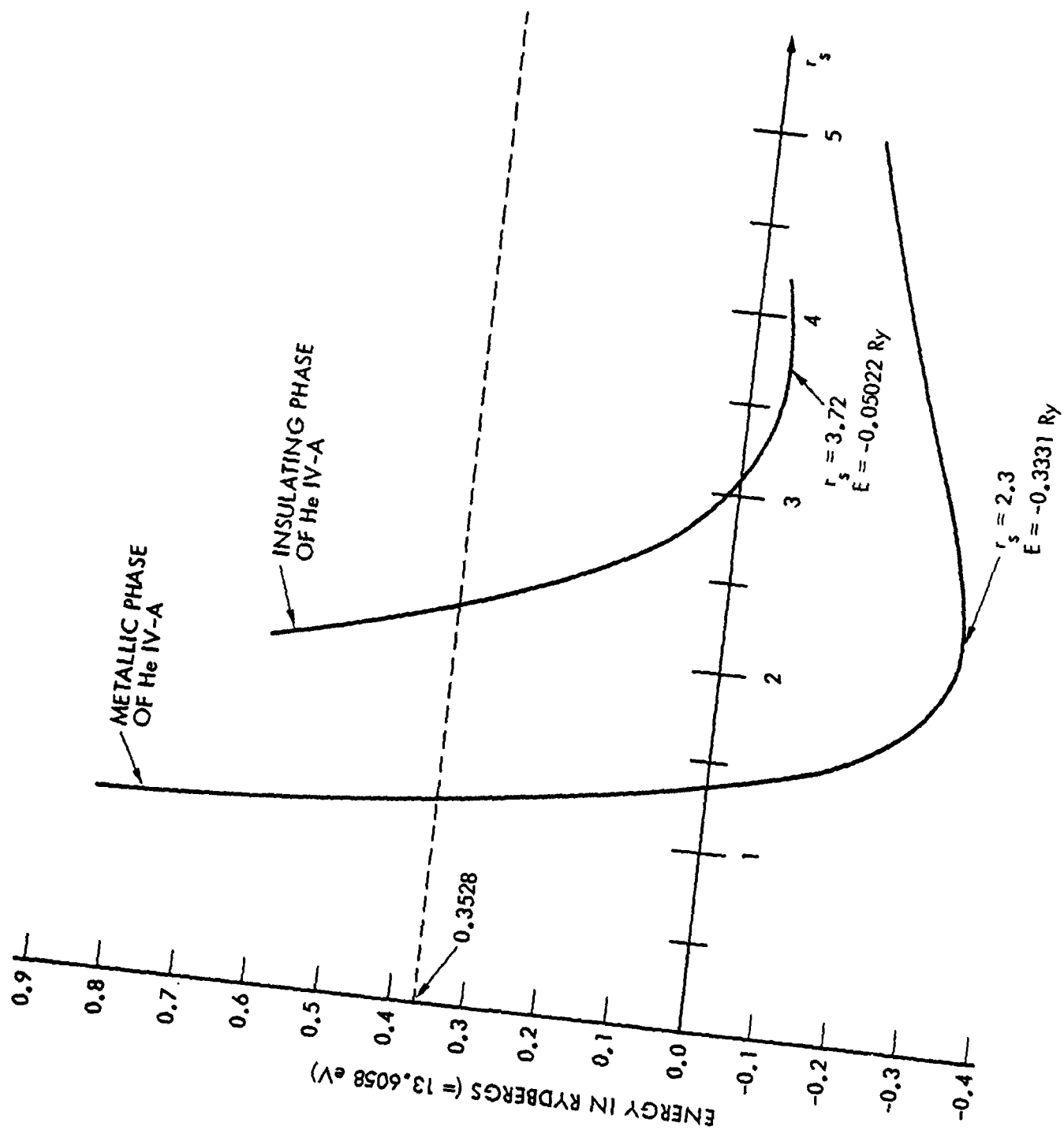
FIG. 3. Energy per atom or per ion-electron pair for the insulating and metallic phases of He IV-A. The dashed line refers to the energy of a single separated ion-electron pair with respect to the energy of a single  $\text{He}^*$ . Arrows mark the positions of minimal energy for each phase.

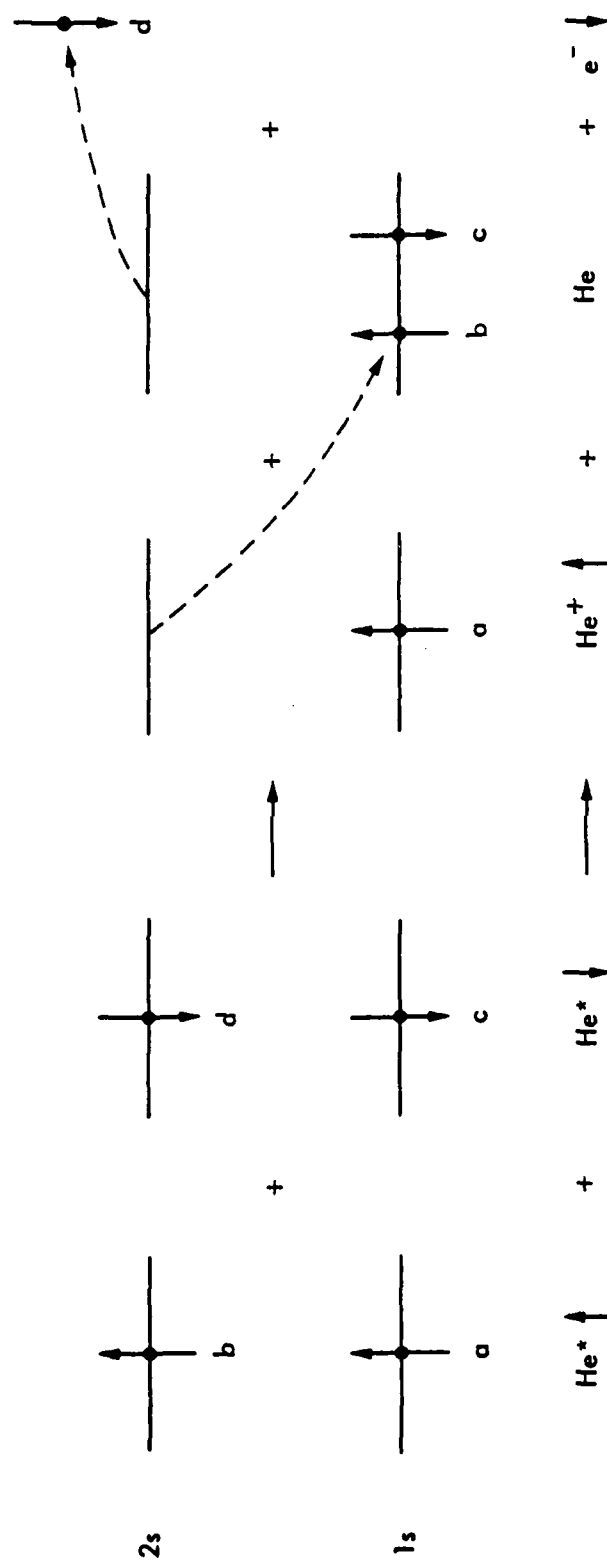
FIG. 4. The mechanism for the autoionizing reaction  $\text{He}^* + \text{He}^* \rightarrow \text{He}^+ + \text{He} + e^-$ , where the initial  $\text{He}^*$  have opposite spins.

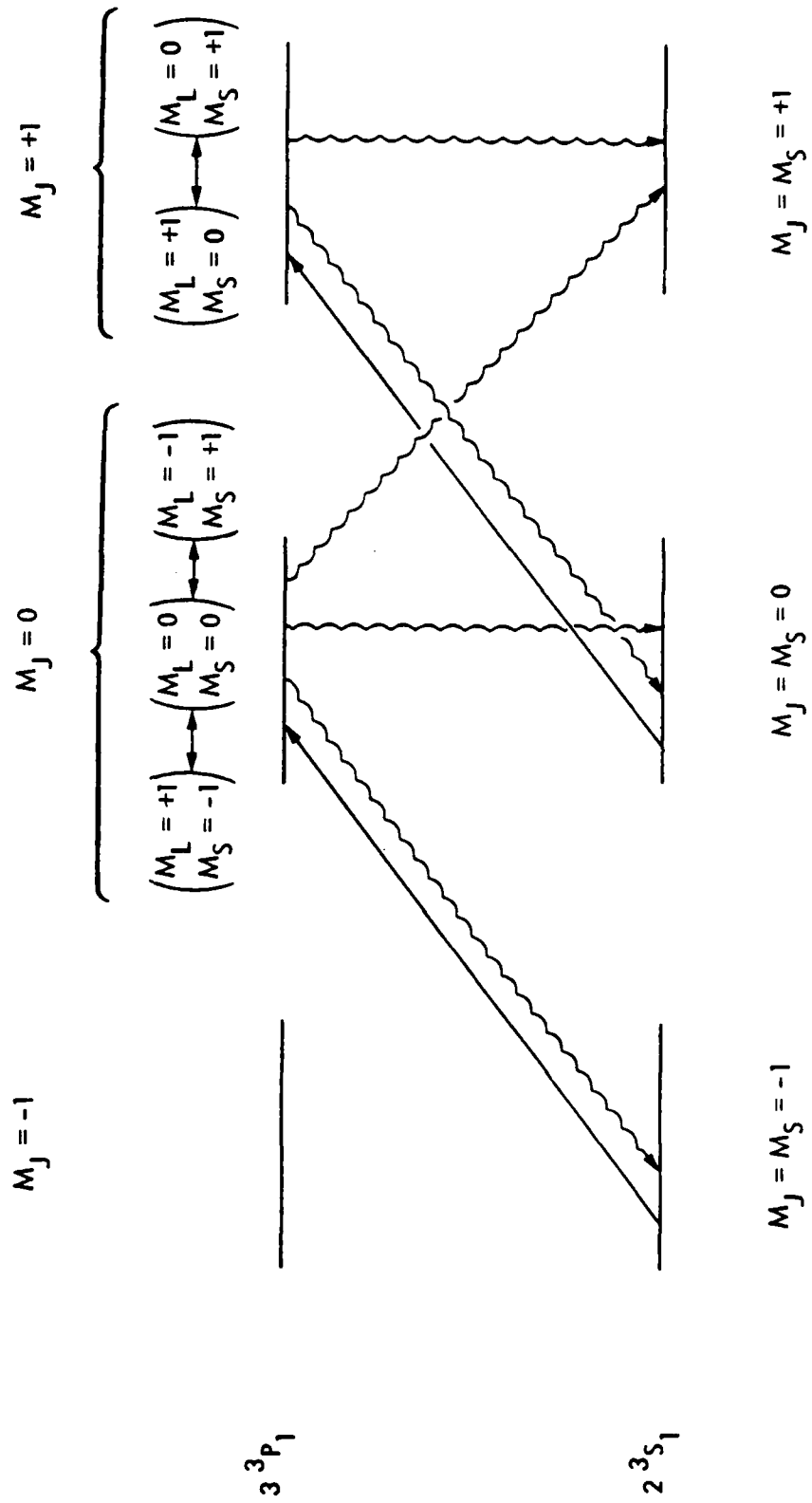
FIG. 5. The optical pumping scheme  $3^3P_1 + 2^3S_1$ . Straight lines indicate E1 pumping transitions induced by 100 % circularly polarized light ( $\Delta m_L = +1$ ,  $\Delta m_S = 0$ ). Wavy lines indicate E1 spin-conserving ( $\Delta m_S = 0$ ) radiative decays from the upper to the lower Zeeman levels. Right-directed, vertical, and left-directed transitions, whether up or down, have  $\Delta m_L = +1$ , 0, and  $-1$ , respectively. Spin-orbit mixing ( $\Delta m_L$ ,  $\Delta m_S \neq 0$  but  $\Delta m_J = 0$ ) in the upper Zeeman levels allows the  $m_J = m_S = +1$  Zeeman level of the  $2^3S_1$  state to be preferentially populated after a number of optical pumping cycles. Weak M1 spin-nonconserving up- and down-transitions are neglected.













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